

SYNTHESIS AND CHARACTERIZATION OF VERMICULITE POLY METHYL METHACRYLATE COMPOSITES

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ABSTRACT

Present manuscript reports the synthesis and characterization of organo vermiculite (OVt) and poly methyl methacrylate (PMMA) composite films by solution blending method. The synthesised OVt-PMMA composite films were characterised using appropriate analytical techniques, like XRD, FT-IR, TG-DTA, SEM, AFM and UTM. The experimental observations reveal the formation of OVt - PMMA composite film with better thermal stability and inhibition in burning behaviour as compared to the pristine PMMA film.

KEYWORDS: OVMT/PMMA Composites, Thermal Stability, Anti - Flammability and Mechanical Properties

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INTRODUCTION

Clay polymers composites have attracted much attention of scientists in recent years, due to their wide range applications e.g., as an adsorbent for the removal of toxic materials from water, as a drug delivery vehicle, as an energy storage device, as a fire retardant material, as a proton exchange membrane in fuel cells and fabrication of automobile parts[1]. Recent studies indicate significant improvement in modulus, strength, gas barrier properties, and heat distortion temperature, of unmodified polymers due to addition of clay [2]. The presence of clay is also reported to impart fire retardant properties due to reduction in heat release, mass loss rate or delayed burning time [3]. Thus many polymeric materials like polystyrene [4, 5, and 6]. Polyvinyl chloride, Nylon [7], polypropylene [8], poly vinyl alcohol [9] are used to prepare fire retardant polymer clay composite [10].

Poly methyl methacrylate (PMMA) is an important thermoplastic material and used as a substitute of inorganic glass. It exhibits excellent properties, like optical transparency, mechanical properties and outstanding dimensional stability [11]. However, its application is restricted in many fields due to its poor thermal stability and conductivity. In order to overcome the problem, different strategies has been adapted, which also includes dispersion of clay particles [12]. It has been reported that incorporation of clay platelets as fillers into PMMA, combines the advantageous properties of clay and PMMA. It offers cost effective and rapid fabrication with a wide range of flexibility, light weight and non-corrosive materials suitable for different applications [13-14]. Further, hydrophilic nature of clay restricts its dispersion for the formation of clay composite. Datta et.al has reported the synthetic methodology for the modification of naturally occurring clay particles with cetylpyridinium chloride to obtain the hydrophobic clay, known as organo clay. The chemically modified clay showed efficient dispersion during composite formation [15].

The aim of this work was to investigate the physical and thermal properties of OVt-PMMA composites, prepared in the solution state, by mixing with different amount of organically modified clay in the PMMA solution. This study demonstrates the optimization of physical and morphological properties (hardness, swelling, thermal stability and burning behaviour) of the PMMA with addition of OVMT clay particles.

EXPERIMENTAL

Materials

High purity Vermiculite was procured from Sigma Aldrich Germany. Poly methyl methacrylate (M.W. 140,000) was purchased from local market, Delhi. The analytical grade tetrahydrofuran (THF) and cetylpyridinium chloride (CPC) were obtained from MERCK- India was used without any further purification.

Modification of Clay

Vermiculite clay was modified by the modification of the reported method [15].

Preparation of Composite

Five gram of poly methyl methacrylate was dissolved in 50ml of THF after constant stirring on a magnetic stirrer at room temperature for four hours. Varying amounts of organoclay was added in the polymer solution and further stirred for 6 hours. Thus obtained translucent solution was poured into borosil petridish (10 cm diameter). The solvent was allowed to evaporate over a period of twenty four hours and a uniform white coloured film was obtained. A reference film of pure PMMA was also prepared by an identical procedure.

Physical Testing

The earlier reported method [16-17] was used for the estimation of solvent content, swelling and porosity of the synthesised composite film. In order to estimate solvent content and degree of swelling, a film specimen with dimension of one cm sq. was cut through a surgical blade; the film was dipped in a beaker containing 100ml of one molar sodium chloride solution for 24 hours. The film was taken out and blotted with the help of a Whatman No. 1 filter paper, the film was weighed immediately after the removal of the surface adsorbed water using Mettler Toledo balance (AB265-5/FACT) with least count of 0.01 mg. The film was again weighed after drying in a vacuum oven. The amount of absorbed solvent content was calculated using the following equation:

$$\text{Solvent content} = \frac{W_w - W_d \times 100}{W_w} \quad (1)$$

Where: W_w = weight of wet film

W_d = weight of dry film

The degree of swelling has been estimated from the difference between the average thickness of the dry film (l_1) and the film soaked in solvent (l_2). The thickness was measured with the help of screw gauge, least count of 0.01mm. The thickness was measured at five different positions and mean value was taken for calculation.

The porosity (E) of composite film was estimated from the volume of solvent incorporated in the cavities per unit of the film present in film. The calculation was made using following equation:

$$E = \frac{W_s - W_d}{AL\delta_w} \quad (2)$$

Where: W_s = weight of film after shocking in solvent

W_d = weight of dry film

A = area of the film

L = thickness of film

δ_w = density of solvent

Flame Retardancy Test

The burning inhibition behaviour of composite film was evaluated by procedure lay down under writer laboratory test (UL-94). The dimension of test specimen and flame were fixed as per recommended conditions of method.

Chemical and Morphological Study

X-ray diffraction patterns were recorded on a Philips X' Pert-PRO PMRD (D8 Discover Bruker AXS, Germany) system using Cu K α radiation ($\lambda = 1.5405 \text{ \AA}$) generated at 40 kV and 40 mA. The diffractogram was recorded between $2-40^\circ$ two theta values with scanning rate $1^\circ/\text{min}$ and step angle $0.02^\circ \text{ s}^{-1}$. The IR spectra were recorded using a Bruker, Model Alpha infrared spectrometer. The IR spectra were recorded in an ATR mode with an accumulation of 16 scan and a resolution of 4 cm^{-1} in the range of 4000 cm^{-1} to 500 cm^{-1} . The microscopic pictures were taken with the help of TESCAM, MIRA-3, Scanning Electron Microscope (SEM) and PARK- XE 100 atomic force microscope (AFM). The images were investigated by scanning over the region of $2 \text{ \mu m} \times 2 \text{ \mu m}$ area of the film.

The composite films were coated with gold using vacuum evaporator in order to avoid charge accumulation prior SEM analysis. The thickness of gold coating was in the range of 10 micrometer.

The thermal stability was investigated by Perkin Elmer, (Pyris diamond) TGA/DTA instrument in the temperature range of ambient to 600°C under the continuous flow of 200 ml/min N_2 flow and heating rate 5°C/min . The temperature of instrument was calibrated with indium metal, while mass loss with standard dehydrated calcium oxalate. Further mechanical properties were measured using INSTRON 3369, Universal Testing Machine with maximum load of 50KN.

RESULTS AND DISCUSSIONS

XRD Pattern

XRD pattern of the PMMA, OVt-PMMA composite and OVt are represented in Figure 1. The diffraction pattern of composite indicates the presence of representative diffraction peaks of OVt in the theta range between 3° to 40° with shift in the peak position with respect to the OVt suggesting intercalation of polymer in the interlayer region of OVt. The amorphous nature of the composite material further suggests irregular arrangement of clay platelets in the polymer matrix [21].

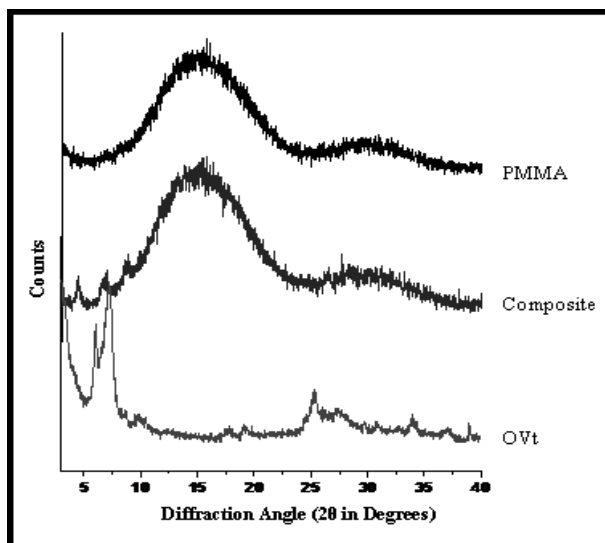


Figure 1: XRD Pattern of PMMA, OVt-PMMA Composites and OVt

FT-IR Analysis

FTIR spectra of Vt, OVt, pure PMMA and OVt-PMMA composite are represented in Figure 2. The absorption bands of Vt at 3328 cm^{-1} has been assigned to OH stretching vibration of interlayer water and silanol group. The vibrational band at 1640 cm^{-1} is due to OH bending vibration of water molecule. The strong vibration band observed at 954 cm^{-1} has been assigned to Si-O-Si and Si-O-Al stretching vibration. The band at 665 cm^{-1} is due to Si-O deformation. In FT-IR spectrum of OVt, the absorption bands at 2917 cm^{-1} and 2850 cm^{-1} have been assigned to asymmetric and symmetric vibration of methylene group of CPC present on the surface of OVt. The vibration bands at 1488 cm^{-1} and 1470 cm^{-1} are due to bending vibration of methylene group which further confirms the presence of CPC on the surface of OVt. [18-20]

In FT-IR spectrum of pure PMMA, the absorption bands at 2996 cm^{-1} , 2917 cm^{-1} and 2856 cm^{-1} have been assigned to C-H asymmetric and symmetric stretching of CH_3 and CH_2 group and the band at 1384 cm^{-1} is due to the bending vibration of CH_2 group present in PMMA polymer. The vibrational band at 1724 cm^{-1} is due to C=O group of PMMA and the band at 1140 cm^{-1} is due to C-O stretching vibration. The band at 986 cm^{-1} relates to syndiotactic arrangement of the branching of PMMA [22-24].

In FT-IR spectrum of OVt-PMMA composite, the disappearance of broad band at 3328 cm^{-1} (due to OH stretching vibration of interlayer water and silanol group), 1640 cm^{-1} (OH bending vibration of interlayer water molecule) and 954 cm^{-1} (Si-O-Si and Si-O-Al stretching vibration) confirms the interaction of PMMA with OVt to form OVt-PMMA composite.

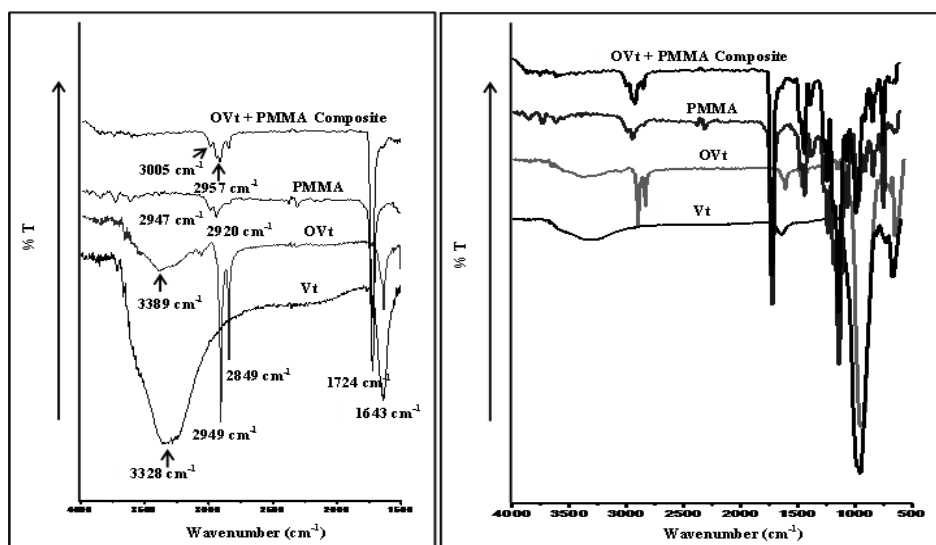


Figure 2: FTIR Spectra of PMMA, OVMT-PMMA Composites and OVMT

Thermal Study

The thermal stability of PMMA and OVt - PMMA composites has been investigated by TG-DTA technique. Both PMMA and its composites shows two step weight loss from 125-220 °C and 300-420 °C along with a significant endothermic peak centered around 275°C.

The initial weight loss of 10% in the range of 125-220 °C is associated with the loss of solvent molecules [25]. The second step with a weight loss of 90% and 85% represents the decomposition of polymer chain in the PMMA and polymer chain along with the surfactant in OVt- PMMA composite respectively. It is obvious from the TG of OVt - PMMA composite that a total of 95% weight loss is observed after thermal degradation as compared to the 100% total weight loss in case of PMMA and is due to the presence of non-combustible residual oxides obtained from the Vt [26].

The position of DTA peaks at 260 and 270 °C represents endothermic process for PMMA and OVt-PMMA composite. The area under the peaks were utilised to compare the heat enthalpy of PMMA and OVt-PMMA composite and it was observed that the presence of Vt in the PMMA matrix brings about higher thermal stability of the OVt- PMMA composite as compared to the pristine PMMA. This may be because the OVt has sheet like structure, which supports the expansion in polymer matrix and hence it need more energy and thus stability of composite enhances [1].

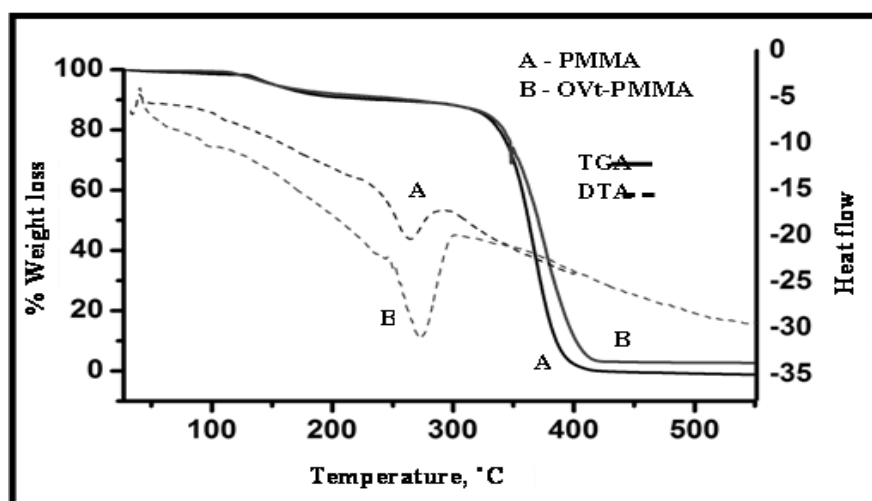


Figure 3: Thermo Gram of PMMA and OVt-PMMA Composite [Identifications]

SEM Images

SEM micrograph of OVt (Figure 4 a) indicates plate like structure with average particle size of 3-7 microns. SEM micrograph of PMMA (Figure 4 b) indicates an uneven continuous morphology with some granules in the range of 0.05- 1 micron size. However, a clear indication of binary morphology with fine granules of clay in range of 0.5-2 microns is observed in case of OVt- PMMA composite film (Figure 4 c). The roughness of the surface of the PMMA film also increases with the addition of Vt. The increase in the roughness of the OVt- PMMA composite film may be due to the different orientation of the Vt platelets within the composites as filler materials. The reduction in clay size is due to the separation of clay sheets during course of dispersion of clay in polymer matrix.

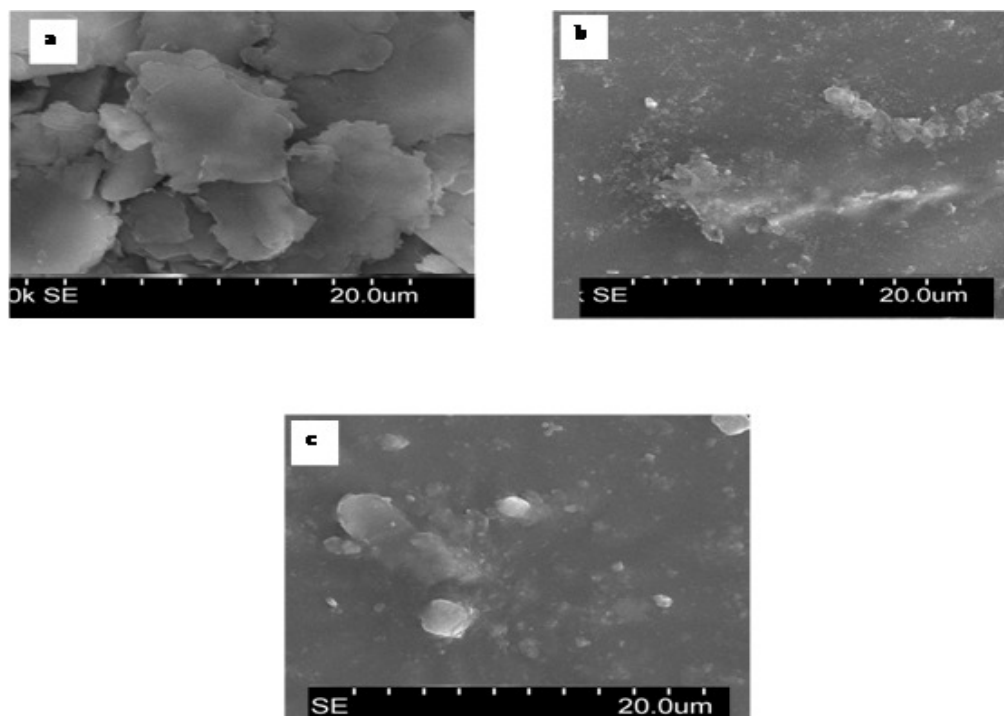


Figure 4: SEM images of (a) OVt, (b) PMMA and (c) OVt-PMMA Composites

AFM Topography Images

Figure 5 (a-d) shows the AFM topographs of the pristine PMMA film and OVt-PMMA composite film and data are listed in Table 2. The pictures support the inference made by SEM for dispersion of clay and size reduction during composite for formation. The addition of clay also resulted increase in roughness of composite after addition of clay.

Increase in the roughness of the OVt- PMMA composite, suggested immiscibility of OVt platelets with the polymer or the filler materials (OVt) of different size are embedded in the PMMA matrix. Which indicates the result for the roughness of the composite materials was increase by double of the pristine PMMA. [27]

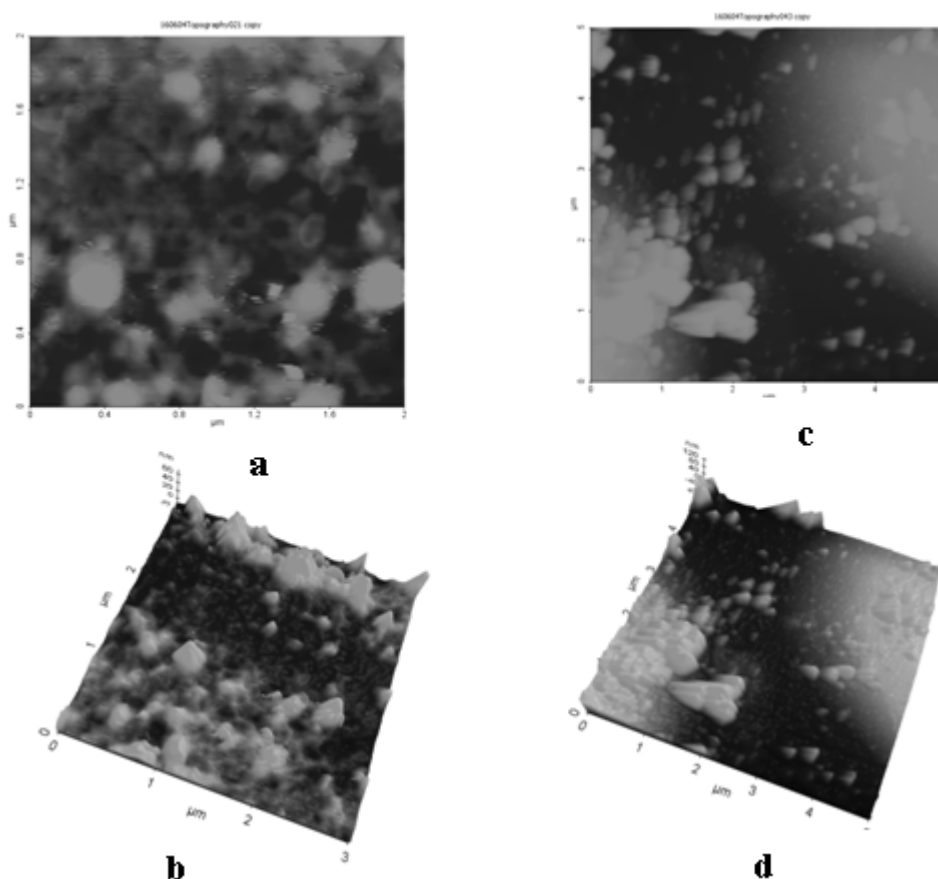


Figure 5: AFM Images for Samples (a) PMMA (Phase) (b) PMMA (Height) (c) OVt-PMMA composite (Phase) (d) OVt-PMMA Composite (Height)

Table 2: Surface Roughness of Pristine PMMA and OVt- PMMA Composites

| Properties | Pure PMMA | OVt- PMMA Composite |
|------------------------------------|-----------|---------------------|
| Max height (nm) | 70.290 | 125.078 |
| Root mean square roughness Rq (nm) | 7.257 | 31.573 |
| Mean roughness Ra (nm) | 4.143 | 25.360 |

The porosity, swelling and solvent absorption studies are also indicating the optimization in matrix during composite formation. The result shown in Table 3- reveals the significant changes in porosity, amount of absorb solvent and swelling behaviour.

Table 3: The Physical Properties of OVMT- PMMA Composite Film and Pure PMMA Film

| Sample | Porosity | Solvent Content Per Unit Volume (cm ³) in mg | (%) Swelling Behaviour |
|--------------------|----------|--|-------------------------|
| Pure PMMA | 2.025 | 0.3081 | 1.5402 |
| OVt/PMMA Composite | 1.067 | 0.8455 | 1.0498 |

Burning Behaviour

The flame retardant data of composite and pristine PMMA are shown in Table 4. It clearly disclosing the increase in flame retardency of poly methyl methacrylate after making its composite with OVt. The flame inhibition capacity was evaluated by comparing the ignition times and was found to be 1.68 time's flammability inhibition in PMMA. It may be because of the layered structures of clay required more energy to expand its matrix on pure PMMA which inhibits burn rating of PMMA.

Table 4: Flammable Behaviour of PMMA and PMMA OVMT Composite

| Sample | Time to Ignite (Second) | Ignition of cotton |
|--------------------|-------------------------|--------------------|
| Pure PMMA | 28.91 | No |
| OVt/PMMA Composite | 49.32 | No |

Mechanical Properties

Results of stress and strain curves of PMMA and OVt/PMMA composite are shown in in Table 5. It indicates the increase in elastic behaviour of polymer due to dispersion of clay particle, which result the increase in extension, stress at maximum load and modulus. It also supports the effectiveness of composite formation and effect of clay dispersion in PMMA matrix.

Table 5: Tensile Stress and Strains of PMMA and PMMA OVMT Composite

| Properties | PMMA | OVt-PMMA |
|--|-----------|-----------|
| Maximum Load (kN) | 0.19123 | 0.16557 |
| Tensile extension at Maximum Load (mm) | 2.31624 | 2.52092 |
| Modulus (Automatic) (MPa) | 538.34109 | 641.23583 |

CONCLUSIONS

A flame retardant OVt/PMMA composite film has been prepared by solution blending process under optimised conditions. The analytical data indicates the advancement in mechanical, physical and anti-flammability properties over the pristine PMMA. The surface morphological study confirms dispersion of OVt plates in to PMMA matrix.

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